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SURFACE PHOTOREACTIONS OF 2-BENZOYLCYCLOPENTANONES: SILICA GEL SURFACE AS A POSSIBLE FIELD BRINGING OUT THE LATENT REACTIVITY OF DISPERSED MOLECULES

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Irradiation of 2-benzoyl- and 2-(*p*-methylbenzoyl)cyclopentanone (1a and 1b), which have the lowest n,π^* excited states and showed no photoreactivities in inert solvents, neat or in the solid state, gave two types of products on a silica gel surface; one arose from the cleavage of the C—C bond *α* to the benzoyl group and the other arose from the cyclopentanone C-1—C-2 bond cleavage. Analysis of Langmuir adsorption isotherm of 1a by a non-linear least-squares method revealed that $7{\cdot}9\times10^{-4}$ mol of 1a was spread as a monomolecular layer over 1 g of silica gel. The photoreactivity of 1a on the surface was very sensitive to the coverage; the efficiency of disappearance of 1a decreased monotonically from 100% at low coverages to zero at nearly 100% coverage. Close packing of molecules of 1 on the surface diminished the photoreactivity. A silica gel surface provided a possible dispersion field for bringing out the latent photoreactivity of 1.

INTRODUCTION

Selectivity in organic reactions is of considerable importance in synthetic and industrial chemistry, and any general technique by which the course of a reaction may be modified is worthy of attention. Photoreactions of organic compounds on solid supports, such as silica gel and alumina, have received much attention because a non-reactive solid surface can provide an ordered two-dimensional environment for effecting and controlling photochemical processes.[1–3] Recently, we have observed that 2-(*N*,*N*-dialkylamino)ethyl 3-benzoylacrylates underwent *E–Z* photoisomerization, competing with other possible photoreactions mainly through remote hydrogen transfer to ketone carbonyl oxygen in solution[4] and only *E–Z* photoisomerization on a silica gel surface, and suggested that photochemical processes requiring comparatively much more conformational mobility are suppressed on the surface since the mobility of the molecules is greatly restricted in the adsorbed state.[5] However, the types of photoreactions observed on the surface are fundamentally the same as those seen in solution,[6] although large differences in the product distributions have been observed in some cases.[5,7] There are various examples of photoreactions which take place only on the surface.[8] In the photochemistry of 2-benzoylcyclohexanones on silica gel we have found that the compounds showed a different photochemical behavior from that observed in solution; the Type I reaction, the products from which could not be expected in the normal reaction course, and the Type II reaction occurred on the surface,[9] although exclusively the Type II reaction occurred in solution.[10,11] The Type I reaction may be general in the photochemistry of 2-benzoylcycloalkanones on the surface. When organic molecules are adsorbed on the surface at a low coverage, the molecules may be free from mutual interactions and are expected to show latent photoreactivities. We have studied the photochemical behavior of 2-benzoylcyclopentanones, which do not show any photoreactivity in inert solvents, on a silica gel surface. We report here on the novel surface photoreaction of the cyclopentanones via the Type I reaction from the upper excited state and on possible use of the surface as a new reaction field for dispersed organic molecules.

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EXPERIMENTAL

Silica gel (Merck Kieselgel 60, Art. 7734) was used as received. IR spectra were recorded with a JASCO IR Report-100 or JASCO FT-IR-7000 spectrometer and the UV spectra with a JASCO UVIDEC-505 spectrometer. The a ^1H and ^{13}C NMR spectra were measured with a JEOL FX90Q or a Bruker AM400 spectrometer using tetramethylsilane as an internal standard. GLC analysis was performed with a Shimadzu GC-8A gas chromatograph. A Taika 100 W or Ushio 450 W high-pressure mercury lamp was used as an irradiation source. The 2-benzoylcyclopentanones **1a–c** were prepared according to the method given in the literature.[12]

General procedure for preparative photolysis of **1** *on a dry silica gel surface.* Compound **1** (*ca* 2·5 mmol) in 5 cm^3 of dichloromethane was added to 5 g of silica gel in a 50 cm^3 round-bottomed flask. The mixture was sonicated for 5 min and the solvent was evaporated under reduced pressure. The coated silica gel was divided into six nearly equal portions and then the portions were placed in Pyrex tubes (18 × 180 mm). The tubes were rotated and irradiated for 48 h with a 100 W high-pressure mercury lamp. The irradiated silica gel was collected in a 100 cm^3 beaker. Acetone (20 cm^3) was added for extraction of organic components. The mixture was sonicated for 10 min. The silica gel was separated by filtration and washed with 10 cm^3 of acetone. The filtrate and washings were combined and then the solvent was removed under reduced pressure. More than 95% of organic materials based on the weight of starting ketone used was recovered by this method. Benzene (20 cm^3) was added to the residue. The mixture was sonicated for 5 min and then allowed to stand for another 5 min. Undissolved material was collected and recrystallized from acetone–hexane to give glutaric acid (**3**). The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel. Elution with acetone–hexane (1 : 6) gave the unreacted starting ketone **1** and photoproducts **2** and **4**. The yields are summarized in Table 1.

The structures of photoproducts **2a**, **2b**, and **3** were determined by direct comparison with commercially available materials. Purification of the **4** could not be achieved because it changed gradually into **5**. Compounds **5a** and **5b** were purified by recrystallization from dichloromethane–hexane. The peaks of carboxyl protons in the ^1H NMR spectra of **5a** and **5b** could not be observed because of highly probable strong line broadening.

Table 1. Product yields in photoreaction of **1** on silica gel

Compound	R	Yield[a] (%) 2	3	4	Conversion[b] of **1** (%)
1a	H	32	35	23	36
1b	Me	26	25	19	42
1c	OMe	0	0	0	2

[a] Based on starting cyclohexanone **1** consumed.

[b] Based on **1** recovered.

5-Benzoyl-5-pentanolide (**4a**): colorless viscous liquid; IR (neat), 1700 and 1750 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·8–2·3 (4H, m, 3-H_2 and 4-H_2), 2·60 (2H, t, $J = 6·9$ Hz, 2-H_2), 5·90 (1H, t, $J = 5·3$ Hz, 5-H) and 7·3–8·0 (5H, m, aromatic); ^{13}C NMR ($CDCl_3$), δ 17·2 (t), 24·5 (t), 29·5 (t), 79·2 (d), 128·7 (d), 129·0 (d, 2C), 133·8 (s), 134·0 (d, 2C), 169·8 (s) and 195·2 (s).

5-Hydroxy-5-benzoylpentanoic acid (**5a**): m.p. 117–118 °C; IR (KBr), 1700, 1720, 3080 and 3450 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·6–2·0 (4H, m, 3-H_2 and 4-H_2), 2·39 (2H, t, $J = 7·2$ Hz, 2-H_2), 3·63 (1H, bs, OH), 5·10 (1H, dd, $J = 5·1$ and 11·3 Hz, 5-H) and 7·5–7·9 (5H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 20·4 (t), 33·2 (t), 34·9 (t), 72·7 (d), 128·6 (d), 128·9 (d, 2C), 133·4 (s), 134·1 (d, 2C), 178·.0 (s), and 201·7 (s); MS *m/z* 222 (M+); Found, C 64·73, H 6·08; calculated for $C_{12}H_{14}O_4$, C 64·85, H 6·35%.

5-(p-Methylbenzoyl)-5-pentanolide (**4b**): colorless viscous liquid; IR (neat), 1700 and 1750 cm^{-1}; ^1H NMR ($CDCl_3$),δ 1·8–2·4 (4H, m, 3-H_2 and 4-H_2), 2·42 (3H, s, Me), 2·61 (2H, t, $J = 7·1$ Hz, 2-H_2), 5·86 (1H, t, $J = 5·3$ Hz, 5-H) and 7·2–7·9 (4H, m, aromatic); ^{13}C NMR ($CDCl_3$), δ 17·3 (t), 21·6 (q), 24·7 (t), 29·6 (t), 79·3 (d), 128·9 (d, 2C), 129·7 (d, 2C), 131·6 (s), 145·0 (s), 169·6 (s) and 194·7 (s).

5-Hydroxy-5-(p-methylbenzoyl)pentanoic acid (**5b**): m.p. 78–78·5 °C; IR (KBr), 1700, 1720, 3080 and 3450 cm^{-1}; ^1H NMR ($CDCl_3$), δ 1·5–2·1 (4H, m, 3-H_2 and 4-H_2), 2·37 (2H, t, $J = 6·2$ Hz, 2-H_2), 2·42 (3H, s, Me), 3·78 (1H, bs, OH), 5·06 (1H, dd, $J = 5·7$ and 12·5 Hz, 5-H) and 7·2–7·8 (4H, m, aromatic); ^{13}C NMR ($CDCl_3$), δ 20·6 (t), 21·6 (q), 33·4 (t), 35·1 (t), 72·7 (d), 128·7 (d, 2C), 129·5 (d, 2C), 131·4 (s), 144·8 (s), 178·0 (s) and 201·2 (s); found, C 65·94, H 6·86; calculated for $C_{13}H_{16}O_4$, C 66·09, H 6·83%.

Photolysis of **1a** *on silica gel at different coverages.* One gram of silica gel and 5 cm^3 of dichloromethane containing appropriate amounts of **1a** were placed in a 50 cm^3 round-bottomed flask. The mixture was sonicated for 5 min and then the solvent was evaporated under reduced pressure. The coated silica gel was placed in a Pyrex tube (18 × 180 mm). The tubes were rotated and irradiated for 48 h with a 100 W high-pressure mercury lamp. After irradiation, 5 cm^3 of acetone containing a known amount of *n*-pentadecane (*ca* 0·2 mmol) as a calibrant for GLC analysis was added. The mixture was sonicated for 10 min. The supernatant solutions were analysed to determine the amount of the unreacted ketone with a gas chromatograph equipped with flame ionization detector using a 2 m column packed with 3% SE30. The results are shown in Figure 1.

Langmuir adsorption isotherm of **1a**. Solutions of hexane–benzene (30 : 1, 5 cm^3) containing appropriate amounts of **1a** were placed in Pyrex tubes (15 × 150 mm) and 0·1 g of silica gel was added to each tube. The tubes were sonicated for 5 min and then allowed to stand for 24 h in the dark. The supernatant solutions were analysed with a UV spectrometer to determine the amounts of **1a** not adsorbed on the silica gel. The results are shown in Figure 2.

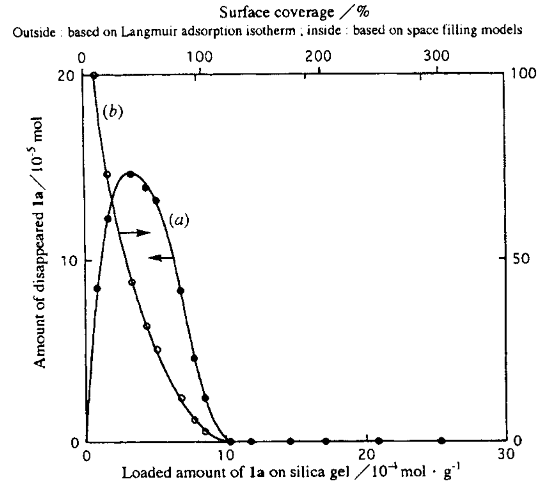


Figure 1. Dependence of extent of disappearance (a) and conversion percentage (b) of the starting material on loaded amounts in the surface photoreaction of **1a**. A 1 g amount of silica gel was used in all runs

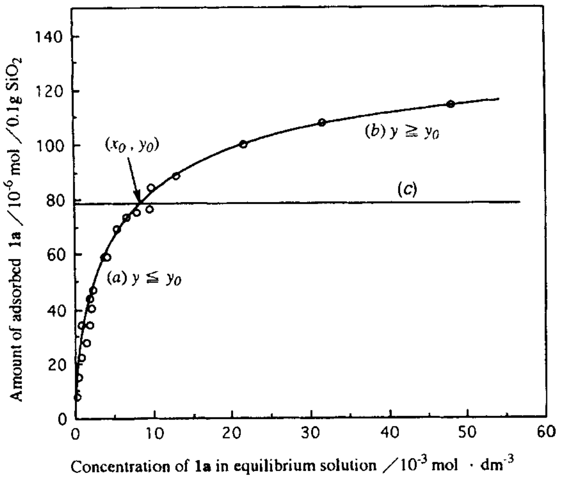


Figure 2. Langmuir adsorption isotherm of **1a**. A 0·1 g amount of silica gel was used for all runs. Line (a) $y = 35x/(1 + 0{\cdot}3x)$, $y \leq y_0$; (b) $y = 3{\cdot}1(x - x_0)/[1 + 0{\cdot}06(x - x_0)] + y2_0$, $x_0 = 9{\cdot}7$, $y \geq y_0$; (c) $y = y_0 = 79$

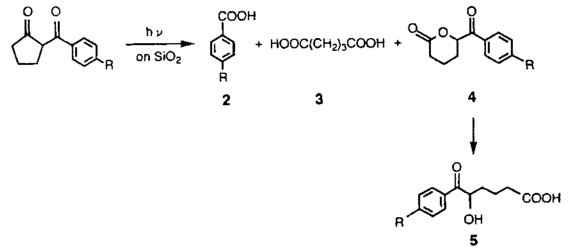
RESULTS AND DISCUSSION

Irradiation of 2-benzoylcyclopentanone (**1a**) on dry silica gel with a 100 W high-pressure mercury lamp gave benzoic acid (**2a**), glutaric acid (**3**) and 5-benzoyl-5-pentanolide (**4a**) in 32, 35 and 23% yields, respectively. The IR spectrum of **4a** showed peaks due to lactone and ketone carbonyls at 1750 and 1700 cm^{-1}, respectively. Complete purification of **4a** could not be achieved because it was a viscous liquid and not very stable, changing gradually into the open-chain compound **5a**. The structure of **5a** was determined on the basis of spectral data and elemental analysis. The IR spectrum of **5a** showed two strong peaks attributable to acid and ketone carbonyls at 1720 and 1700 cm^{-1}, respectively, a sharp peak due to a secondary alcohol at 3450 cm^{-1} and a wide peak characteristic of a carboxylic acid centered at 3080 cm^{-1}. The mass spectrum showed the weak parent peak at a mass number of 222. Formation of **5a** can be reasonably explained in terms of lactone ring opening of **4a** by addition of water. Formation of benzoic acid (**2a**) and glutaric acid (**3**) can be explained in terms of the α-cleavage as in the surface photoreaction of 2-benzoylcyclohexanone.[9] In the surface photoreaction of the cyclohexanone, no lactone corresponding to **4a** was detected. The lactone **4a** is the characteristic product of the surface photoreaction of the cyclopentanone **1a**. It is worth noting that the silica gel surface provided a new reaction environment for **1a** because **1a** did not show any photoreactivity in inert solvents, neat or in the solid state. Formation of **4a** can be reasonably explained in terms of the reaction *via* the oxacarbene produced from the α-cleavage of the cyclopentanone C-1—C-2 bond. This α-cleavage should occur from the upper cyclopentanone carbonyl excited state, although the α-cleavage producing **2a** and **3** should take place from the lowest benzoyl carbonyl excited state. Thus, the two types of α-cleavage occurred in the photoreaction of **1a** on the surface. The photoreaction from an equilibrating upper triplet state has been reported in ketones having energetically proximate excited states.[13] However, the exthothermic energy transfer should proceed much faster than chemical reactions.[14] Then, photochemical reactions generally take place from the lowest excited states. The fast exthothermic energy transfer could be possible in benzoylcyclopentanone (**1a**) because the energy difference between triplet excited state of cyclopentanone ($E_T \approx 80$ kcal mol^{-1})[15] and that of acetophenone ($E_T = 74$ kcal mol^{-1})[16] is fairly large. The competition of the normal C—C cleavage α to the benzoyl group with the abnormal cyclopentanone C-1—C-2 bond cleavage is, therefore, a rare event. The restriction of molecular motion on silica gel is known to cause an increase in the triplet lifetimes of some aryl alkyl ketones.[17] The restriction of molecular motion might also decrease the rate of interconversion of the excited state energy across two carbonyl groups in **1a** and makes it possible that photoreactions occur from two different excited states, that is, the benzoyl and the cyclopentanone carbonyl n, π^* states.

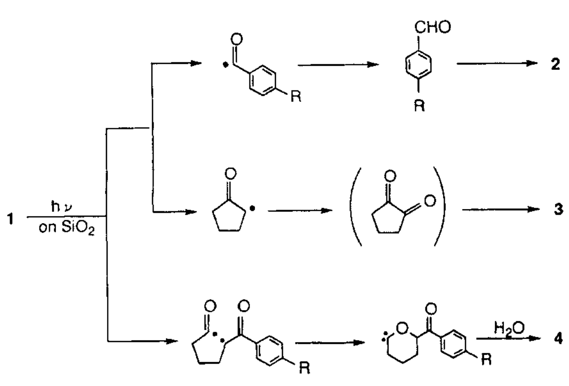
Similarly, irradiation of 2-(*p*-methylbenzoyl)cyclopentanone (**1b**) on the surface gave **2b**, **3** and the lactone **4b** in 26, 25 and 19% yields, respectively. However, when 2-(*p*-methoxybenzoyl)cyclopentanone (**1c**) was irradiated under the same conditions, no photoproduct could be obtained. The lowest excited state of **1c**, as for *p*-methoxyacetophenone and *p*-methoxyvalerophenone,[13] is probably the π, π^* state. Therefore, the photoreactions of **1a** and **1b** on the silica gel surface producing **2a** and **2b**, respectively, and **3** proceed from their n, π^* state. Lack of the photoreaction from the upper state probably due to the larger extinction coefficient at >300 nm and the lower E_T energy of the anisoyl group than the benzoyl group.[13]

Reaction schemes are shown in Schemes 1 and 2.

The ^{1}H NMR spectra of **1a** and **1b** in $CDCl_3$ showed that *ca* 60% of molecules of these compounds exist in enol forms. The lack of photoreactivity of these compounds in solution is probably due to the strong internal filter effect by the enol forms.[10,18] The photoreactions of **1a** and **1b** must occur from their keto forms. The silica gel surface possessing silanol OH groups[1] should provide a polar reaction environment and enhance the keto contents[6d] of **1a** and **1b**. Indeed, the FT-IR spectrum of **1a** adsorbed on the silica gel surface [50 mg of **1a** on 1 g of SiO_2; 34% coverage (see discussion below)] showed evidence for an increase in the keto form; the peaks at 1605 and 1630 cm^{-1}, which are very strong in the neat form and attributable to the enol chromophore, became weak and the peaks at 1675 and 1740 cm^{-1}, which are relatively weak in the neat form and attributable to the keto chromophore, became very strong. The increase in the keto contents should enhance the photoreactivity of **1a** and **1b**. However, this seems to be a minor factor for the observed photoreactions of **1a** and **1b** because 90% of the starting material was recovered after 48 h of irradiation of **1a** in methanol and no evidence for the production of **2a**, **3**, or **4a** could be obtained from the analysis of the irradiated solution.



Scheme 1



Scheme 2

The internal filter effect should be trivial in surface photochemistry when all loaded molecules are in the monomolecular layer. The coverage of the molecules on the surface must be an important factor for surface photoreactions because the character of the reaction environment changes at 100% coverage. The effect of surface coverage on the photoreaction of **1a** was studied using samples loading different amounts of **1a** on 1 g of silica gel. Line (a) in Figure 1 shows the relationship between the amount of **1a** loaded on the silica gel and the amount of **1a** that disappeared under the same irradiation conditions. The amount of **1a** that disappeared increased initially with an increase in the loaded amount, reached a maximum and then decreased. These results suggest that the surface coverage influenced on the photoreactivity of **1a**. Therefore, we studied the nature of **1a** adsorbed on silica gel.

The monolayer coverage can be determined from the Langmuir adsorption isotherm[7a,7c,8,19] or by calculation based on the surface area of 1 g of silica gel and the area occupied by one molecule of **1a** determined from space-filling models.[6c,7c,8,9] In the analysis of the Langmuir adsorption isotherm, graphical methods have often been used.[7a,8] The amount of an adsorbate at the crossing point of two lines, which are obtained from the linear relationship between the amount of the adsorbate and concentration of equilibrium solution in low and high concentration regions,[7c] or at the *y*-intercept of the extrapolated line in the high concentration region,[7a] is just required to make the monomolecular layer on silica gel. The values estimated from the isotherm and by calculation using space-filling models sometimes show good agreement.[7c,8] However, drawing of lines in the graphical methods may give an intentional result because the slopes of the lines, especially in the low concentration region, depend on the number of data used. We therefore devised a non-linear least-squares method to estimate the amount of the adsorbate required for the formation of a monolayer by using a simple adsorption model.

The Langmuir adsorption isotherm was obtained by using 0·1 g of silica gel (Fig. 2). Adsorption of molecules to the molecules already adsorbed on the silica gel surface to make a second layer probably takes place after completion of the monomolecular layer if the interaction between molecules is weaker than that between molecules and the surface and multilayers could not be formed when the number of molecules on the first layer is small. If this is the case, the Langmuir adsorption isotherm can be analysed by the following equations:

$$y = \begin{cases} \dfrac{bx}{1+ax} & \text{when } y \leqslant y_0 \qquad (1) \\[2ex] \dfrac{d(x-x_0)}{1+c(x-x_0)} + y_0 & \text{when } y \geqslant y_0 \qquad (2) \end{cases}$$

where x is the concentration of equilibrium solution, y is the amount of adsorbate on silica gel, x_0 and y_0 are the concentration and amount at completion of the first layer and a, b, c and d are parameters.

Initially, the amount required for the monomolecular layer (y_0) was tentatively estimated to be the value obtained from the y-intercept of the extrapolated line in the high concentration region. The experimentally obtained data were divided into two groups on the basis of the amount of the adsorbate on silica gel (y) larger and smaller than y_0. The curve fittings by using the non-linear least-squares method were performed separately for these two different data groups. Then, the y_0 value was slightly changed and the new value was used as the y_0 value. The experimental data were classified again into two groups as described above and the curve fittings were repeated. The determination of the new y_0 value and the curve fitting were repeated until the square of errors between the experimental and the calculated values was minimized. The experimentally obtained data in the figure fit curves with $x_0 = 9{\cdot}7 \times 10^{-3}$ mol dm^{-3}, $y_0 = 7{\cdot}9 \times 10^{-5}$ mol, $a = 0{\cdot}34$, $b = 35$, $c = 0{\cdot}06$ and $d = 3{\cdot}1$. Therefore, the amount of **1a** needed to make a monomolecular layer on 1 g of silica gel was determined to be $7{\cdot}9 \times 10^{-4}$ mol. A close value ($8{\cdot}4 \times 10^{-4}$ mol) was obtained by using space-filling models.

The coverage at the turning point where the photoreaction of **1a** ceased was nearly 100%. The coverage at the maximum of line (a) in Figure 1 is *ca* 40%. The relationship between the conversion percentage of **1a** loaded on the silica gel surface and the coverage is shown by line (b) in Figure 1. These results suggest that a close approach of molecules of **1a** diminishes the photoreactivity and that the silica gel surface provides a dispersion field for the photoreaction of **1a**. Prevention of the photoreaction by the close approach of molecules of **1a** may be due to a deactivation process resulting from contact of molecules.

In conclusion, a silica gel surface provides a possible dispersion field for bringing out the latent photoreactivity of organic molecules. Upon irradiation on silica gel, 2-benzoylcyclopentanones having the lowest n, π^* excited state, which showed no photoreactivity in inert solvents, neat or in the solid state, underwent photoreactions in two modes of α-cleavage to give an arylcarboxylic acid, glutaric acid and a 5-aroyl-5-pentanolide when the surface coverage was less than 100%. The restriction of molecular movement on the surface probably allows the photoreactions from two different excited states, aryl carbonyl and cyclopentanone carbonyl excited states, because of the decreased interconversion of the excited state energy across two carbonyl groups.

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